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Publicized Report of Patent

DETAILED REPORT

(Name of the invention)

Plasma display and manufacturing method for the same

Outline

(Object)

This invention offers a plasma display which prevents detachment of the ends of the cell walls and also has no accidental electric discharge at the edges. Furthermore, this invention offers a plasma display which has uniform intensity over its whole surface.

(Solution)

This object can be attained by a plasma display, where a dielectric layer and stripe shaped cell walls are formed on the substrate. This plasma display has an inclined section on the long ends of the cell walls. In addition, the manufacturing method for a plasma display in this invention is attained by using a paste for the cell walls which consists of inorganic materials and an organic component. Stripe shaped cell walls which have an inclined part the end are formed on the substrate. The material is sintered to then form the stripe shaped cell walls.

Sphere of patent request

(claim 1)

Claim 1 is regarding a plasma display which has the following characteristics: A dielectric layer and stripe shaped cell walls are formed on the substrate. This plasma display has an inclined section on the ends of the lengthwise direction of the cell walls.

(claim 2)

Claim 2 is regarding the plasma display in claim 1 which has the following characteristics : the height of the inclined part (Y) and length of the bottom side of the inclined part (X) in the cell walls are in the range below:

$0.5 \leq X / Y \leq 100$

(claim 3)

Claim 3 is regarding the plasma display in claim 1 or 2 where the length of the bottom side of the inclined part (X) is 0.05 to 10 mm.

(claim 4)

Claim4 is regarding the plasma display in claims 1 to 3 where the inclined angle is 0.5 to 60 degrees.

(claim 5)

Claim 5 is regarding a manufacturing method for the plasma display in claims 1 to 4 which has the following characteristics. A paste for cell walls which consists of inorganic

materials and an organic component is used to form stripe shaped cell walls which have inclined ends on a substrate. The cell wall material is sintered to form cell walls which have an inclined part on the ends in the lengthwise direction.

(claim 6)

Claim6 is regarding a manufacturing method for the plasma display in claim 5 which has the following characteristics. After forming a film coating by applying paste for cell walls on the substrate so that it has an inclined surface on the ends, a stripe shape cell wall pattern is formed so that the inclined surface of the coating will be the ends of the cell walls in the lengthwise direction. The cell wall material is sintered, and stripe shaped cell walls are formed.

(claim 7)

Claim 7 is regarding the manufacturing method for the plasma display in claim 5 which has the following characteristics. After forming a coating by applying paste for cell walls on the substrate, an inclined surface is formed by processing the coating, and stripe shape cell walls are formed so that the inclined surface of the coating will form the end section in the lengthwise direction. The cell wall material is sintered, and stripe shaped cell walls are formed.

(claim 8)

Claim 8 is regarding the manufacturing method for the plasma display in claims 5 to 7 which has the following characteristics. The paste for cell walls is a photo-sensitive material. During the process which forms the cell wall pattern, the coating of paste for cell walls is exposed to light through a photo mask which has a stripe shaped pattern longer than the coating length which has an inclined surface at the ends. After it is developed, a stripe shaped cell wall pattern is formed.

(claim 9)

Claim 9 is regarding the manufacturing method for the plasma display in claims 5 to 8 where the height (Y') of the inclined part before sintering, the length (X') of the inclined part, and the shrinkage rate (r) during sintering have the following relationship:

$$0.5 \leq X' / (r \times Y') \leq 100$$

(claim 10)

Claim 10 is regarding the manufacturing method for the plasma display in claims 5 to 9 where the height (Y') of the inclined part before sintering is 0.2 to 1 times the height of the cell walls before sintering.

(claim 11)

Claim 11 is regarding the manufacturing method for the plasma display in claims 5 to 10 which has the following characteristics. A dielectric paste which consists of inorganic materials and an organic component is coated on the substrate. After forming a stripe shaped cell wall

pattern using the other paste for forming the cell walls, the above dielectric paste film and cell wall pattern are sintered at the same time.

Detailed explanation of invention

[0001]

(Technical field of this invention)

This invention is concerning a plasma display and its manufacturing method. This plasma display can be used for big TV or computer monitors.

[0002]

(Prior art)

A plasma display (PDP) has high speed compared to a liquid crystal panel, and it is also easy to make in a large size. Therefore, it is used in the field of OA equipment, information display devices, etc. In addition, development into the field of high definition TV is very much expected.

[0003] With the growing demand for larger devices such as the above, a color plasma display which has fine resolution and many display cells has been gaining attention. To explain the AC plasma display, for example, a plasma electric discharge is produced between opposing anodes and cathodes inside the electric discharge space between the front glass substrate and back glass substrate. UV rays produced by the gas sealed inside the electric discharge space irradiate a layer of luminous material inside the electric discharge space. This processes makes a display. Figure 1 is a simple figure which shows the construction of an AC plasma display. The electric discharge is contained in a fixed area and the display is illuminated inside the regulated cell. At the same time, in order to form a uniform electric discharge space, cell walls (blocking walls, also called ribs) are set up. In the case of an AC plasma display, these cell walls are formed into stripes.

[0004] The cell walls above are approximately 30 to 80 μm wide and 70 to 200 μm high. Normally, an insulating paste which includes glass powder is screed printed and dried on the front glass substrate or back glass substrate. This process is repeated more than 10 times in order to form cell walls with the desired height.

[0005] Japan patents No. H 1-296534, No. H 2-165538, No. H 5-342992, NO. H 6-295676, No. H 8-50811 suggest a method of forming cell walls using a photo-sensitive paste by photo lithography technique.

[0006] In any of the above methods, cell walls are made by forming insulating paste which includes glass powder into a cell wall pattern and sintering it. The ends of the cell walls release from the base due to shrinkage difference between the upper and lower part of the cell walls during sintering as shown in figure 4. As shown in figure 5, although it may not release, there have been problems where the upper part of the cell walls swell up.

[0007] When this releasing at the ends of the cell walls occurs, when the panel is formed by pasting the front and back boards together, gaps are produced between the tops of the cell walls and the back and front plates. Because of these gaps, cross talk is produced during electric discharge, which causes disturbances in the screen image.

[0008] A method of solving this problem is suggested in Japan patent No. H 6-150828. In this method, the composition of the upper and lower layers is changed by making the cell walls a multi-layer structure. Glass with a lower melting point is used in the lower layer. In addition, Japan patent No. H 6-150831 suggests a method which sets up a glass foundation layer under the ends. However, none of these methods is sufficient to prevent releasing of the cell walls at the ends. Japan patent No. H 6-150832 discusses a method which makes the ends of the cell walls step-shapes. However, this is also insufficient to prevent for preventing releasing of the cell walls at the ends.

[0009]
(Problems that this invention tries to solve)

The object of this invention is to offer a highly precise plasma display which eliminates the releasing of the cell walls at the ends and a manufacturing method for the same. This invention also offers a highly precise plasma display which has much less accidental electric discharge and a manufacturing method for the same. The plasma display in this invention works by electric discharge inside the electric discharge space which is separated by cell walls. In addition to the above AC plasma display, this invention includes various kinds of electric discharge displays starting with plasma address liquid crystal displays.

[0010]
(Steps for solving the above problems)

The object of this invention is to offer a plasma display where a dielectric layer and stripe shaped cell walls are formed on a substrate. This plasma display has an inclined section at the ends of the lengthwise direction of the cell walls.

[0011] The object of this invention is attained by a plasma display where a dielectric layer and stripe shaped cell walls are formed on a substrate. This plasma display has an inclined section at the ends of the lengthwise direction of the cell walls. The manufacturing method for the plasma display in this invention uses a paste for the cell walls which consists of inorganic materials and an organic component. A stripe shaped cell wall pattern with an inclined part on the ends is formed on the substrate. The cell wall pattern is sintered to form the stripe shaped cell walls.

[0012]
(State of practice of this invention)

In this invention, it is necessary that ends of the cell walls be inclined. Having an inclined part at end parts of cell walls means that at least part of the end of the cell wall is tapered as shown in figure 2. By having an inclined part on the ends of the cell walls as shown in figure 2, it is possible to relieve stress due to adhesion and shrinkage-induced stresses in the upper part of the cell walls. This prevents releasing of the cell walls from the substrate.

[0013] If there is no inclined part on the ends of the cell walls, the top of the cell walls can shrink freely during sintering, as shown in figure 3, while the lower part of the cell walls is bonded to the foundation. It is assumed that de-bonding (figure 4) or deformation (figure 5) occurs due to the difference in this shrinking stress.

[0014] Any shape can be used for the inclined part, such as a concave curve (2), convex curve (3), or multiple straight lines (4).
[0015] Furthermore, an inclined should be formed on both ends of the cell walls in order to prevent an uneven gap between the front and back plates when the panel is sealed.
[0016] An inclined part can also be combined with a step as shown in figure 6. However, the height of the step should be less than 50 μm. Since a step which makes a right angle cannot balance shrinking stress, there is a tendency for the wall to rise up as height increases or the slope increases. If it is less than 50 μm, the rise is small. When a panel 20 inches or more is formed, the front plate and cell walls are attached, and cross talk is difficult. When a step and an inclined part are combined, the inclined part should be set up on the highest part of the cell walls. If an inclined part exists at the highest part, rising up can be prevented.
[0017] The height (Y) of the inclined part and the length (X) of the bottom side of the inclined part are in the range indicated below.
[0018] $0.5 \leq X / Y \leq 100$
The length (X) of the bottom of the inclined part should be in the range of 0.05 to 50 mm. Since the inclined part is lower than the desired height of the cell walls it produces a disturbance in the screen image, so X should not exceed 50 mm. It is better if it is 10 mm or less, or 5 mm or less is best. In addition, if it is less than 0.05 mm, its effect in preventing rising is small.
[0019] Furthermore, in this invention, the inclined angle of the cell walls should be in the range of 0.5 to 60 degrees. When the incline is not a straight line, as shown in figure 8, the maximum angle is adopted as the inclined angle. If the inclined angle is less than 0.5 degrees, since the inclined part is too long, it is not good for the panel design. On the other hand, if the inclined angle is more than 60 degrees, peeling off during sintering cannot be sufficiently controlled. A desirable range is 20 to 50 degrees.
[0020] Since debonding and rising up occur at during sintering, the inclined part should be formed before sintering the cell walls.
[0021] The shrinkage rate during sintering is called "r". Shrinkage hardly occurs in the lengthwise direction of the cell walls although it is remarkable in the direction of height. If the height of the inclined part before sintering is called Y' and the length of the inclined part is called X', $Y = r \times Y'$, $X = X'$. Accordingly, in order attain a pattern of cell walls after sintering in the range of size in this invention, the cell wall pattern before sintering should be in the range of $0.5 \leq X' / (Y' \times r) \leq 100$.
[0022] If the height Y' of the inclined part before sintering is 0.2 to 1 times the height of the cell walls before sintering, it will be effective for preventing rising up of the end part of the cell walls. If it is less than 0.2 times as much, it is impossible to relieve the difference in shrinkage stress between the upper and lower parts of the cell walls, and it will not prevent swelling. If the height is equal, depending on the process used to form the inclined part, there are cases when the dielectric or electrode set up on the substrate is damaged. The height ratio should be 0.9 less. Preferably, it is in the range of 0.3 to 0.8.
[0023] Measurement of the shape of the inclined part can be done by any suitable method. However, it should be done using an optical microscope, scanning electron microscope, or laser microscope.

[0024] For example, when a scanning electron microscope (HITACHI S-2400) is used, the following method is preferred. First, the sample is sectioned so that the ends of the cell walls will show up accurately, and it sized for observation. The area where the incline comes into view is selected for magnification. After the scale is edited to show a standard sample the same size as the inclined part, a photo is taken. The length of X and Y is measured by the method shown in figure 7, and the shape is calculated from the scale.

[0025] When a non-destructive measurement is desired, it is possible to use a laser focus displacement measurer (for example, LT-8010 manufactured by Keyence). In this case also, the measurement should be done after editing with a standard sample. The measurement surface of the laser must be parallel to the stripe direction of the cell walls in order to perform an accurate measurement.

[0026] The manufacturing method for the plasma display in this invention consists of the following: A paste for cell walls which consists of inorganic materials and an organic component is used to form a stripe shaped cell wall pattern which has an inclined part on the ends on the substrate. This cell wall pattern is sintered to forming the stripe shaped cell walls. Although the method used to form the inclined part on the end of the cell walls is not specifically limited, the following methods can be used.

[0027] One of these methods is as follows. A glass paste for the cell walls is applied to the substrate so that the edge of the coating forms the inclined surface. The cell wall patterns are formed so that the inclined surface of the coating will be the end of the lengthwise direction of the stripe shape cell wall pattern. Although the application method is not specifically limited; screen printing, roll coating, doctor blade coating, or slit die coating which spouts from a cap are preferred.

[0028] The cell wall pattern can be formed by screen printing method, sand blasting method, lift-off methods, photo lithography, etc.

[0029] In the case when the cell wall pattern is formed by photo lithography, the stripe shaped cell wall pattern is formed by exposing the coating with the inclined surface through a photo mask which has a stripe shaped pattern and developing it. By exposing it to light through a photo mask which has a stripe shaped pattern longer than the coating, it is possible to acquire a stripe shaped cell wall pattern with the inclined part at the ends. This method does not require post-processing. The inclined part can be formed without additional process steps.

[0030] Another method is going to be explained next. According to this method, after the glass paste for cell walls is applied on the substrate, the inclined surface is formed by processing the coating. A cell wall pattern is formed so that the inclined surface of the coating will be the end in the lengthwise direction of the stripe shaped cell walls.

[0031] Any method can be used to form the inclined surface on the coating. However, a preferred method of forming the inclined surface is by propelling liquid onto the coating. Specifically, fluid is propelled onto the coating while it is still fluid and before it is not completely dried and cured. The inclined surface is formed as shown in figure 9.

[0032] Any fluid can be used in this method, as long as it is liquid or gas at working temperatures. However, it should be a substance which does not remain on the substrate after sintering also which can perform the task cleanly. A gas is preferred because it is clean and it does not require collection. Although the gas components are not specifically limited, air or

nitrogen are favorable due to their low cost. W gas is used, it should be propelled onto the coating to form the inclined surface while the coating is not totally dried and cured and still has fluidity. Another preferred fluid is solvent. When solvent is used, precise processing is possible by forming the inclined surface after drying and curing the coating.

[0033] A nozzle or slit should be used for propelling the fluid. The inner diameter of the nozzle or area of the slit should be 0.01 mm to 3 mm. If it is less than 0.01 mm, the necessary flow cannot be attained, and the inclined surface cannot be formed. On the other hand, if it exceeds 3 mm, controlling the position of the fluid jet becomes difficult.

[0034] Mechanical methods can also be used to form the inclined surface on the coating. These mechanical methods include using an edge tool, a whetstone (hone), or similar tools, sand blasting, or laser irradiation. The amount of material removed depends on the thickness of the coating, and 10 to 90 % of the coating thickness is preferred. 50 to 80 % is good. If too much material is removed, there are concerns that it may sharpen the substrate. On the other hand, if too little material is removed, there will be areas that are not sharpened due to uneven thickness of the coating. Sharpening should be done after drying and curing the coating in order to prevent rising up due to sharpening. In addition, it is possible to use this method after curing by heat or UV. It can be also applied when parts are partially cured by photo lithography methods after exposing the pattern to UV.

[0035] The material removal rate can be determined by watching the sharpened surface. 0.05 to 10 mm/min. is preferred.

[0036] If an edge tool or grinding tool is used, any materials which are commonly used as sharpening materials such as ceramics, high speed steel, or super-steel, can be used.

[0037] When the coating is made by applying a photo-sensitive paste as in the case where the cell wall pattern is formed by photo lithography method, the sharpening should be done before development and after exposing. Sharpening waste can be washed away by the development process, and it is possible to prevent problems caused by sharpening waste easily.

[0038] When the lift-off method is used to form the cell wall pattern, the resin mold and paste for cell walls should be ground simultaneously after filling the paste for cell walls in a resin mold and drying and curing it. By sharpening simultaneously, it is possible to prevent falling of the cell wall pattern. In addition, since sharpening waste can be removed in the mold removal process, it helps prevent problems. The lift-off method means the following method. First, a resin mold is formed as the mother mold of the cell wall pattern on a glass substrate by a photo-sensitive resin, and it is filled with paste for cell walls. Next, after the paste for cell walls is dried, the resin mold is removed, and the cell wall pattern is formed. By sintering the cell wall pattern, cell walls are formed.

[0039] When sand blasting is used to form the cell wall pattern, after removing the unnecessary part by sand blasting, it is acceptable to sharpen it using a resist layer. Since sharpening waste can be removed simultaneously when the resist layer is removed, it prevents problems. Sand blasting means the following method. First, a resist layer is applied on the paste for cell walls. By exposing the resist layer to light and developing it, a cell wall pattern mask is formed. The cell walls are formed by removing the unnecessary part by sand blasting. After that, the resist layer is removed, the cell wall pattern is sintered, and the cell walls are formed.

[0040] One example of a desirable shape for the edge of the coating where the surface has been sharpened is shown in figure 10. The height of the part which is not the inclined part is t1, the coating thick is t2, and the angle of the inclined surface is ϕ. The following range is desired: $t1 / t2 = 0.1$ to 0.8, $\phi = 0.1$ to 60 degrees. Because of this, you can use an edge tool, a whetstone that matches the shape of the inclined surface (for example, the shape shown by the broken line in figure 10). You can either move the edge tool or whetstone while the substrate is fixed, or move the substrate while the tool is fixed. When an edge tool is used, a side view is shown in figure 11 and figure 12. In the figures, the edge tool is fixed while the substrate moves in the direction of the arrow. The angle between the edge tool and the substrate can be set either facing the substrate as shown in figure 11 or covering the substrate as shown in figure 12. It is selected according to the characteristics of the coating. In either case, the angle Θ between the edge tool and the substrate is in the range of 10 to 80 degrees, especially 15 to 60 degrees.

[0041] In the case of sharpening by sand blasting or by laser, the angle of sand blasting and laser irradiation becomes important. These angles can be set to fit the shape of the inclined surface. The angle can be 0.1 to 60 degrees the same as the above.

[0042] The sharpening waste should be removed with force. Forceful removal of the sharpening waste should be done by absorbing the sharpening waste. Doing so prevents re-attaching of the waste to the surface of the coating, and it will prevent defects in the panel. In addition, the absorbing pressure of the device which used for absorbing should be in the range of 10 to 500 hPa.

[0043] Furthermore, it is acceptable to change the relative position of the edge tool or whetstone with respect to the coating depending on the desired coating profile so that the shape of the coating will be always fixed. When the cell wall pattern is formed on a glass substrate which has more than 20 inches in diagonal, undulation on the order of several tens of µm exists on the substrate. Fixing the distance between the edge tool or whetstone and the substrate prevents sharpening the dielectric or electrode, and it will prevent defects.

[0044] It is possible to process the coating to form the inclined surface with solvent. Specifically, the solvent is contained in cloth, and the inclined surface is formed by rubbing the coating. In addition, it is possible to form the inclined surface by pressing a wedge shaped stamp on the coating.

[0045] When the cell wall pattern is formed by photo lithography, as stated above, a photo mask is used. This mask has a stripe shaped pattern that is longer than the coating. Using the long mask, it is possible to acquire a stripe shaped cell wall pattern which has the inclined part at ends.

[0046] The length of the coating includes the length of the inclined surface. If part of the coating (called the remaining coating in the following) remains outside the inclined surface, this remaining of coating is not included in length measurement of the coating. This remaining coating is removed from the substrate in a post-process such as development, etc. For example, figure 9 shows the inclined surface. The left side is the coating, and the right side is outside the coating. In this invention, the part left of the dotted line is regarded as the end of the coating. The part to the right of the dotted line at the right is unnecessary coating. The photo mask should be longer than the coating including the inclined surface, but this length does not include the remaining coating. In other words, by using a photo mask where the end of the pattern exists between the

dotted lines in the figure, the remaining coating is not exposed. Therefore, it is removed by the development process, and a cell wall pattern which has the inclined part at the end is attained.

[0047] It is also possible to form the inclined part after forming the cell wall pattern. However, because it is easy and requires fewer process steps as stated above, the cell wall pattern should be formed after forming the inclined part.

[0048] The following is another method of forming the inclined part at the ends of the cell walls. The mother mold with stripe shaped grooves is filled with paste for cell walls that consists of inorganic materials and an organic component. This molded paste is transferred to a substrate and sintered at 400 to 600°.

[0049] That is, in this method, grooves that correspond to the cell wall pattern are formed in the mother mold beforehand. The mold is filled with the glass paste for cell walls. The molded paste is transferred to a glass substrate to form the cell wall pattern. In this method, the cell wall pattern is transferred from the mold to a glass substrate. By applying pressure during this transfer, defects can be prevented. In addition, application of heat makes releasing the paste from the mother mold easy. When the organic component in the glass paste contains a component which is polymerized by heat, since it produces a volume change due to polymerization shrinkage, release of the cell wall pattern from the mold is easy.

[0050] In this invention, it is possible to form the inclined part at the ends of the cell wall pattern by the methods described above after cell wall pattern has been formed. However, if the inclined parts at the ends of the grooves are formed in the mother mold beforehand, it is possible to form the inclined part without increasing the number of process steps, which is desirable.

[0051] Another method is the following method. The paste for cell walls that consists of inorganic materials and an organic components is pressed onto the substrate. The cell wall pattern is formed by pressing the mother mold with stripe shaped grooves onto the coating. The cell wall pattern is sintered at 400 to 600°.

[0052] This method forms the cell wall pattern by uniformly applying the glass paste for cell walls on part of the surface of the glass substrate beforehand and then pressing the mother mold onto this layer of paste. The method used to apply the glass paste to the glass substrate uniformly is not limited specifically. For example, screen printing, die coating, or roll coating can be used.

[0053] In this method, it is also better to form the inclined part at the ends of grooves in the mother mold beforehand.

[0054] Figure 13 is a section of the mother mold which is suitable for the manufacturing methods described above. It has inclined part at the ends of the grooves in the mother mold. Polymer resin or metal can be used to form the mother mold. However, in the first manufacturing method, a mother mold made of silicon rubber can be used. In the later manufacturing methods, a mother mold manufactured by pattern etching or pattern polishing which uses a metal polishing agent can be used.

[0055] In addition to having the inclined part at the edges, the cell walls can be a multi-layer construction which uses a low-softening point glass in the lower layers to improve adhesion. By improving adhesion to the foundation, deformation can be prevented.

[0056] When the width of the lower surface is Lb, the half-height width is Lh, and the width of the upper surface is Lt, the that cell walls for plasma display in this invention should be in the following range.

Lt / Lh = 0.65 to 1
Lb / Lh = 1 to 2

Also, Lb is the width of the bottom of the cell walls, Lh is the half-height width, and Lt is the width of the upper part of the cell walls.
[0057] If Lt / Lh is bigger than 1, it will produce a constriction in the center of the cell walls and the ratio of electric discharge area to the cell wall pitch, in other words, the opening rate becomes small and luminosity drops. In addition, it produces uneven thickness or erratic coverage in the luminous later. On the other hand, if Lt / Lh is less than 0.65, the upper surface becomes too thin, and the wall strength is insufficient to withstand the pressure difference when the panel is evacuated. Damage to the top edge easily occurs. When Lb / Lh is less than 1, strength is low, and it this is a factor for wall damage, etc. If Lb / Lh is bigger than 2, luminosity drops since the electric discharge area is reduced.
[0058] A better range of Lt / Lh = 0.8 to 1, Lb / Lh = 1 to 1.5 for securing the opening rate. However, if Lt = Lh = Lb, the walls are weak and damage easily occurs. A trapezoidal shape or rectangular shape which does not have a constriction in the lower surface of the cell walls is preferred because of strength.
[0059] Making the cell wall pattern before sintering in these shapes increases contact area between the substrate glass or dielectric layer, and shape retention and stability is improved. As a result, problems with delamination after sintering and broken wires can be prevented.
[0060] The porosity of the cell walls in this invention should be less than 10 % to prevent cell wall damage and to provide superior bonding to the substrate. Less than 3 % is even better. Porosity (P) is defined as P = (d th – d ex) / d th x 100 when the true weight of the cell wall materials is d th, and the measured density of the cell walls is d ex.
[0061] The true weight of the cell wall materials should be calculated using Archimedes' principle. The cell wall materials should be ground with a mortar and pestle so that grains can't be felt by touch, that is, to less than 325 mesh or so. Next, the true weight is found as stated in JIS – R 2205.
[0062] Next, actual density is measured by removing the cell walls so that the shape will not be damaged. The material is not ground, and the same procedures as above are used. Measurement is done using Archimedes' principle.
[0063] When porosity is more than 10 %, in addition to a loss in adhesion, it will be cause for insufficient strength, loss in light-emitting characteristics such as luminosity due to absorption of moisture or gas losses. Considering the desired functional life span of the panel and light-emitting features such as stable luminosity, 1 % or less is even better.
[0064] In the case when it is sued for cell walls of plasma display or plasma address liquid crystal display, because pattern formation is done on glass substrate with low glass transition point, softening point, it is preferred to use glass materials with 430 to 500 °C glass transition point and 470 to 580°C softening point as cell walls materials. If glass transition point is higher

than 500°C and softening point is higher than 580°C, it is necessary to sinter at high temperature. So, warping (curve) is produced at substrate at sintering. On the other hand, materials with glass transition point lower than 430°C and softening point lower than 470°C cannot acquire tight cell walls layer. This will cause delamination, broken wires, etc.

[0065] It is preferred that measurement of glass transition point, softening point is done as follows. Using differential thermal analysis (DTA) method, approximately 100 mg of glass sample is heated in air at 20°C/min. Temperature is plotted at a cross axis, and calorie is plotted at vertical axis, and DTA curved line is drawn. According to DTA curved line, glass transition point and softening point are read.

[0066] Thermal expansion coefficient of general high warping point glass which is used for substrate glass is 80 to 90 x 10^{-7} / K. Therefore, because of prevention of warping of substrate, crack at sealing of panel, it is preferred to use glass materials, of which thermal expansion coefficient ($\alpha_{50\ to\ 400}$) at 50 to 400°C is 50 to 90 x 10^{-7} / K, preferably 60 to 90 x 10^{-7} / K, at both cell walls and dielectric layer. By using glass materials which have the above features, it is possible to prevent peeling of cell walls or cut wire.

[0067] As composition of cell walls materials, it is preferred that silicon oxide is combined in the range of 3 to 60 wt. % in glass. If it is less than 3 weight %, tightness, strength, or stability of glass layer drops. Also, thermal expansion coefficient comes out of desired values, and unfitting with glass substrate is easy to occur. By making it at less than 60 wt. %, there is merit such as that thermal softening point becomes low and marking to glass substrate becomes possible.

[0069] By combining boron oxide in glass in the range of 5 to 50 wt. %, it is possible to improve mechanical and thermal features such as electric insulation, strength, thermal expansion coefficient, tightness of insulation layer. If it exceeds 50 wt. %, stability of glass drops.

[0069] Among of lithium oxide, sodium oxide, and potassium oxide, by using glass powder which contains at least one kind of them for 2 to 15 wt. %, it is possible to acquire photo-sensitive paste which has temperature characteristic that can be pattern-processed on glass substrate. As for alkali metal oxide such as lithium, sodium, and potassium, etc., by making its added amount at less than 15 wt. %, stability of paste can be improved.

[0070] As glass composition which contains lithium oxide, it is preferred to contain the following composition at oxide conversion note:

lithium oxide	2 to 15 wt. %
silicon oxide	15 to 40 wt. %
boron oxide	15 to 40 wt/ %
barium oxide	2 to 15 wt. %
aluminum oxide	6 to 25 wt. %

Also, in the above composition, it is possible to use sodium oxide, potassium oxide instead of lithium oxide. However, lithium oxide is better for the aspect of stability of paste.

[0071] Also, by glass which contains both metal oxide such as lead oxide, bismuth oxide, zinc oxide, and alkali metal oxide such as lithium oxide, sodium oxide, or potassium oxide, control of softening point or linear expansion coefficient becomes easy with even lower alkali containing amount.

[0072] When dielectric layer is set up between substrate and cell walls, compared to the case when it is formed directly on substrate, adhesion of cell walls is increased, and peeling off is controlled.

[0073] As for thickness of dielectric layer, 5 to 20 μm, preferably 8 to 15 μm is preferred for formation of uniform dielectric layer. If thickness exceeds 20 μm, at sintering, taking off if difficult, and crack is easy to occur. In addition, since stress loaded to substrate is high, problems such as substrate is warped will happen. Also, if it is less than 5 μm, it is difficult to maintain uniformity of thickness.

[0074] After cell walls patterns are formed on coating for dielectric layer, if cell wall pattern and coating for dielectric layer are sintered simultaneously, de-binder of cell wall pattern and coating for dielectric layer occurs simultaneously also. Therefore, shrinkage stress by de-binder of cell wall pattern is relieved, and peeling off or cut wire can be prevented. Compared to this, in the case when only coating for dielectric layer is sintered first and then cell wall pattern is formed on top of this and is sintered, peeling or cut wire at sintering due to insufficient bonding between cell walls and dielectric layer is easy to occur. Also, when cell wall pattern and coating for dielectric layer are sintered simultaneously, there is another merit that numbers of process can be less.

[0075] In the case of simultaneous sintering method, if curing of film is performed after coating for dielectric layer is formed, it is preferred since the coating will not be immersed in development solution at process to form cell walls patterns. For curing coating for dielectric layer, photo-sensitive one is used for paste for dielectric layer. After it is applied on glass substrate and is dried, it is exposed to light, and it is cured by light. This method is simple and is used favorably.

[0076] In addition, coating can be cured also by thermal polymerization. In this case, there is a following method. Radical polymerization monomer or radical polymerization initiator is added to paste for dielectric. After this paste is applied, heating is performed.

[0077] It is possible to omit curing of coating for dielectric layer. However, compared to the case in which curing is done, it gets corrosion by development solution at process to form cell walls patterns. In addition, crack is easy to happen in dielectric layer. Accordingly, it is necessary to select insoluble type polymer for development solution.

[0078] As for dielectric layer of this invention, it is desired that it has glass, of which value of thermal expansion coefficient ($\alpha_{50\ \mathrm{to}\ 400}$) at 50 to 400°C is 70 to 85 x 10^{-7} / K, preferably 72 x 80 x 10^{-7} / K, as main component, for the aspect of corresponding to thermal expansion coefficient of substrate glass and reducing stress given to glass substrate at sintering. To have it as main component means that at least 60 wt. %, preferably 70 wt.% or higher is contained in total components. If it exceeds 85 x 10^{-7} / K, stress such as that substrate is warped is given to the side of dielectric layer formed surface. On the other hand, if it is less than 70 x 10^{-7} / K, stress such as that substrate is warped will be loaded to the side where there is no dielectric layer. Because of this, there are cases when substrate is cracked if heating and cooling of substrate are repeated. IN addition, at sealing with the front substrate, there are cases when both substrates do not go parallel because of warping of substrate and cannot be sealed.

[0079] Warping amount the substrate for plasma display in this invention is in inverse proportion to curvature rate radius R of the substrate. Therefore, it can be regulated according to a reciprocal number (1/R) of curvature rate radius of substrate. At this point, positive and

negative value of warping amount indicates direction that substrate is warped. Although curvature rate radius of glass substrate can be measured by various kinds of methods, method to measure undulation on the substrate using surface roughness measurer (Surfcom 1500 A manufactured by Tokyo Seimitsusha, etc.) is the easiest. Warping amount 1/R can be calculated from the maximum deviation H of undulated curved line, measured length L, using following formula.

[0080] $1 / R = 8H / L2$

In the case when warping is produced on substrate, gap will be produced between head part of cell walls and surface of front board at sealing of front board and back board. As a result of that, accidental electric discharge is generated between each cell, and substrate is damaged at sealing. In order to avoid these problems, it is necessary to set absolute value of warping amount to be less than 3×10^{-3} m^{-1}. That is, it is necessary to set warping amount of substrate within the following range.

[0081] $-3 \times 10^{-3}\ m^{-1} \leq 1 / R \leq 3 \times 10^{-3}\ m^{-1}$(R indicates curvature radius of substrate)

In this invention, by not essentially containing alkali metal in dielectric layer, it is possible to prevent warping of substrate at sintering or crack at sealing of panel. In this invention, not essentially containing means that included amount of alkali metal is less than 0.5 wt. %, preferably 0.1 wt. % or less per inorganic materials. Even if thermal expansion coefficient is corresponding to substrate glass, in the case when contained amount of alkali metal, such as Na (sodium), Li (lithium), K (potassium), exceeds 0.5 wt. % in dielectric, ion exchange occurs with glass component in electrode or glass substrate at sintering. Because of this, thermal expansion coefficient in surface part of substrate or dielectric layer changes. So, it will not match with thermal expansion coefficient of substrate and dielectric layer, and pulling stress is produced on substrate, and it will become cause for crack in substrate. In addition, it is preferred that alkali earth metal is not essentially contained either.

[0082] It is preferred that dielectric layer in this invention has at least 2 layers. Two-layer structure of dielectric layer which is formed on electrode on glass substrate (will be called as dielectric layer A) and dielectric layer formed on dielectric layer A (will be called as dielectric layer B) is desired. For example, in the case when silver is used as electrode, component in dielectric layer A and component on glass substrate or silver ion cause reaction such as ion exchange, and there are cases when problems such as that dielectric layer A is colorized happen. Especially, in the case when alkali metal and its oxide is contained in dielectric layer A, this ion exchange reaction occurs considerably, and there are cases when dielectric layer A turns yellow. In order to solve these problems, it is desired that dielectric layer A and B in this invention are inorganic materials which do not essentially contain alkali metal.

[0083] For dielectric layer of this invention, by using glass which contains at least one kind from lead oxide, bismuth oxide, zinc oxide, preferably 10 to 60 wt. % of bismuth oxide, control of thermal softening temperature and thermal expansion coefficient will be easy. Especially, to use glass which contains 10 to 60 wt. % of bismuth oxide has merit such as stability of paste, etc. However, if added amount of lead oxide, bismuth oxide, zinc oxide exceeds 60 wt. %, heat-resistance temperature of glass becomes too low, and marking onto glass substrate will be difficult.

[0084] As example of concrete glass composition, there is one which includes the following composition at oxide conversion indication. However, this invention is not to be limited to only this glass composition.

[0085]

bismuth oxide	10 to 60 wt. %
silicon oxide	3 to 50 wt. %
boron oxide	10 to 40 wt. %
barium oxide	5 to 20 wt. %
zinc oxide	10 to 20 wt.%

As inorganic materials which are contained in dielectric layer of this invention, white color filler such as titanium oxide, alumina, silica, barium titanate, zirconia is used. Inorganic materials which contain 50 to 95 wt. % of glass, 5 to 50 wt. % of filler are used. By containing filler in the above range, reflectivity of dielectric layer is improved, and plasma display with high luminosity can be attained.

[0086] Dielectric layer in this invention can be formed by applying or layering dielectric paste which consists of inorganic material powder and organic binder on glass substrate and sintering it. Amount of inorganic material powder which is used for paste for dielectric layer is desired to be 50 to 95 wt. % per sum of inorganic material powder and organic component. If it is less than 50 wt.%, tightness of dielectric layer, flatness on the surface are lacking. On the other hand, if it exceeds 95 wt.%, paste viscosity goes up, and uneven thickness at application becomes prominent.

[0087] Although manufacturing method of cell walls in this invention is not limited strictly, photosensitive paste method, which has less process and also enables detailed pattern formation, is preferred.

[0088] This photo-sensitive paste method is the following method. Using photo-sensitive paste which consists of inorganic material that has glass powder as its main component and organic material that has photo-sensitive feature, coating is formed. This coating is exposed to light through photo mask, and it is developed. According to this, cell walls patterns are formed. After that, cell walls patterns are sintered, and cell walls are attained.

[0089] As for amount of inorganic materials which are used in photo-sensitive paste method, it is desired that it is in the range of 65 to 85 wt. % per sum of inorganic materials and organic component.

[0090] If it is less than 65 wt. %, shrinkage rate at sintering becomes big, and it will be cause for cut wire of cell walls, peeling off, etc., which is not desired. In addition to that, drying becomes hard as paste, and it sticks, and printing feature drops. Also, swelling of pattern, remaining film at development are easy to occur. On the other hand, if it is bigger than 85 wt. %, since photo-sensitive component is small, photo-curing cannot be done down to bottom of cell walls pattern, and formation of pattern will be bad.

[0091] In the case when this method is used, it is desired to glass powder as follows as inorganic materials.

[0092] By adding aluminum oxide, barium oxide, calcium oxide, magnesium oxide, zinc oxide, zirconium oxide, especially aluminum oxide, barium oxide, and zinc oxide, to glass powder, it is

possible to control softening point, thermal expansion coefficient, and refractive index. However, its contained amount should be less than 40 wt. %, preferably 25 wt.% or less.

[0093] Glass which is generally used as an insulator has a refractive index of approximately 1.5 to 1.9. When the photo-sensitive paste method is used, if the average refractive index of the organic component is largely different from the average refractive index of the glass powder, reflection and scattering at the interface between the glass powder and organic component is large, and detailed patterns cannot be attained. Since the refractive index of organic components is generally 1.45 to 1.7, in order to adjust the refractive index of the glass powder and organic component, the average refractive index of the glass powder should be 1.5 to 1.7, preferably 1.5 to 1.65.

[0094] By using glass which includes 2 to 10 wt. % total of alkali metal oxide such as sodium oxide, lithium oxide, or potassium oxide, etc., not only is control of the softening point and coefficient of thermal expansion easy, it is also possible to lower the average refractive index of the glass. Therefore, it is easy to make the difference in refractive indices small. When it is lass than 2 %, it will be hard to control the softening point. If it is greater than 10 %, luminosity drops due to evaporation of alkali metal oxide during the electric discharge. The amount of alkali metal oxide is less than 8 wt. % in order to improve stability of the paste, preferably 6 wt. % or less.

[0095] Lithium oxide is especially desirable since it can improve the relative stability of the paste. When potassium oxide is used, only a small amount is needed to control refractive index.

[0096] As a result, it is possible to have softening point which enables marking the glass substrate and also to make the average refractive index 1.5 to 1.7. It is easy to make the difference in refractive indices small.

[0097] Glass which includes bismuth oxide is desired for softening point control or improvement of water-resistance. However, glass which includes more than 10 wt. % of bismuth oxide tends to have refractive index higher than 1.6. Because of this, using bismuth oxide and an alkali metal oxide such as sodium oxide, lithium oxide, or potassium oxide together, it is easy to control softening point, coefficient of thermal expansion, water-resistance, and refractive index.

[0098] The refractive index of the glass materials in this invention should be measured ate the wavelength of light which is used to expose the photo-sensitive glass paste in order to confirm its effects. It should be measured at a wavelength in the range of 350 to 650 nm. Furthermore, measurement of refractive index at line i (365 nm) or line g (436 nm) is desired.

[0099] The cell walls in this invention may be colored black to improve contrast. By adding various kinds of metal oxides, it is possible to color the cell walls after sintering. For instance, by adding 1 to 10 wt. % of black metal oxide to the photo-sensitive paste, it is possible to form a black pattern.

[0100] The black metal oxide used may be one, preferably 3 or more of oxides such as Ru, Cr, Fe, Co, Mn, Cu. 5 to 20 wt. % of oxides of Ru and Cu is especially effective in forming a black pattern.

[0101] Using paste which has an inorganic pigment with red, blue, green, etc., color can be used to make a pattern in a color other than black. These colored patterns can be used suitably for color filters for the plasma display, etc.

[0102] The dielectric constant of the cell wall glass material should be 4 to 10 at 1 MHz and 20°C to improve power consumption and discharge life span. In order to make it less than 4, it is necessary to include a lot of silicon oxide, which has a dielectric constant of approximately 3.8. Since the glass transition point becomes high and also sintering temperature becomes high, this may cause warping of the substrate, which is not desired. On the other hand, if it is more than 10, power loss due to increased electrostatic charge occurs, causing increased power consumption, which is not desired.
[0103] The specific weight of the cell walls in this invention should be 2 to 3.3. In order to make it less than 2, a lot of alkali metal oxide such as sodium oxide or potassium oxide is required in the glass material. These oxides are evaporated during electric discharge and are a factor for deterioration of electric discharge characteristics, which is not desired. If it is more than 3.3, when it is made into a big screen the display is heavy or the substrate warps due to its own weight, which is not desired.
[0104] The particle diameter of the glass powder used is selected considering the width or height of the cell walls which will be manufactured. However, the 50 volume % particle diameter (average particle diameter D50) should be 1 to 6 μm, the maximum particle diameter should be 30 μm or less, and the relative surface area should be 1.5 to 4 m^2/g. Preferably, the 10 volume % particle diameter (D10) is 0.4 to 2 μm; 50 volume % particle diameter is 1.5 to 6 μm; 90 volume % particle diameter (D 90) is 4 to 15 μm; the maximum particle diameter is 25 μm or less; and the relative surface area is 1.5 to 3.5 m^2/g. If D 50 is 2 to 3.5 μm and the relative surface area is 1.5 to 3 m^2/g, it is even better.
[0105] D10, D50, and D90 refer to the average particle diameter 10 volume %, 50 volume %, and 90 volume %. To make these measurements, the powder is first sorted starting from the smallest particle diameter.
[0106] If the actual particle size distribution is smaller than the particle distribution above, the relative surface area is increased, and the cohesive force of the powder goes up. Dispersion in the organic component drops, and it is easy to entrain air bubbles. Because of this, scattering is increased, the center of the walls are thicker and the bottom part will not cure sufficiently, and the desired shape cannot be attained. In addition, if the actual particle size distribution is too big, the bulk density of the powder drops, and mold filling is more difficult. As a result, the amount of photo-sensitive organic component becomes insufficient, and it is easy to entrain air bubbles, creating scattering problems.
[0107] Accordingly, there is an optimum particle size distribution. By using glass powder which has the particle size distribution above, filling of powder is improved. Even if the amount of powder in the photo-sensitive paste is increased, there will be fewer air bubbles. Because unnecessary scattering is small, formation of cell wall patterns is maintained. Since the amount of powder is high, the sintering shrinkage rate becomes low. Pattern accuracy is improved and the desired cell wall shape can be attained.
[0108] The method of measuring the particle diameter is not limited strictly, laser diffraction-scattering methods are desired because they are easy. For instance, measurement conditions for a particle size distribution measurer HRA 9320-X100 manufactured by Micro Track are as follows:

[0109] Amount of sample: 1 g, dispersing condition: ultrasound dispersion for 1 to 1.5 minutes in purified water. If dispersion is difficult, it is done in a 0.2 % sodium hexamethalate solution.
[0110] Particle refractive index: this parameter changes according to the type of glass used (lithium base: 1.6, bismuth base: 1.88), solvent refractive index: 1.33, number of measurements: two

It is possible to use 3 to 60 wt. % filler with a softening point of 550 to 1200°C, preferably 650 to 800°C in the cell walls of this invention. By doing so, the shrinkage rate during sintering becomes small in the photo-sensitive paste method. Pattern formation is easy, and there is less deformation during sintering.

[0111] The filler should be a high melting point glass powder which includes at least 15 wt. % of ceramics such as titania, alumina, barium titanate, zirconia, silicon oxide, or aluminum oxide. For example, the glass powder with the following composition can be used.

[0112]

silicon oxide:	25 to 50 wt. %
boron oxide	5 to 20 wt. %
aluminum oxide	25 to 50 wt. %
barium oxide:	2 to 10 wt. %

When high melting point glass powder is used as filler, if the difference in refractive index between the main glass material (low melting point glass) and the filler is large, adjusting with the organic component becomes difficult, and pattern formation will be bad.

[0113] Therefore, when the average refractive index N1 of the low melting point glass powder and the average refractive index N2 of high melting point glass powder are in the following range, adjustment of refractive index with organic component will be easy.

[0114] $-0.05 \leq N1 - N2 \leq 0.05$

It is important that variation in the refractive index of the inorganic powder is small in order to minimize light scattering. Variation in the refractive index should be ±0.05 (95 volume % or more of the inorganic powder is in the range of N1±0.05) to reduce scattering.

[0105] The filler should have an average particle diameter of 1 to 6 μm. The particle size distribution should be D10 (10 volume % particle diameter) is 0.4 to 2 μm; D50 (50 volume % particle diameter) is 1 to 3 μm; D90 (90 volume % particle diameter) is 3 to 8 μm; the maximum particle diameter of 10 μm or less forming ease in forming the pattern.

[0116] It is even better if D90 is 3 to 5 μm and the maximum particle size is 5 μm or less. If D90 is 3 to 5 μm this is a fine powder which reduces shrinkage during sintering and makes excellent cell walls with low porosity. In addition, it is possible to make the unevenness in wall height ±2 μm or less. When powder with big particle diameter is used for filler, not only does porosity go up, but unevenness in wall height, and it causes extraneous electric discharge, which is not desired.

[0117] The organic component contained in the glass paste can be a cellulose compound represented by ethyl cellulose or an acryl polymer represented by polyisobutyl methacrylate. In addition, you can use polyvinyl alcohol, polyvinyl butyral, ester methacrylate polymer, ester acrylate polymer, ester acrylate – ester methacrylate co-polymer, α-methyl styrene polymer, butyl methacrylate resin, etc.

[0118] In addition, it is possible to use various additives in the glass if necessary. For example, if viscosity must be adjusted, organic solvent can be added. The organic solvent can be methyl cellosolve, ethyl cellosolve, butyl cellosolve, methyl ethyl ketone, dioxane, acetone, cyclohexanone, cyclopentanone, isobutyl alcohol, isopropyl alcohol, tetrahydrofuran, dimethyl sulfoxide, γ-butylolactone, bromobenzene, chlorobenzene, dibromobenzene, dichlorobenzene, bromobenzoic acid, chlorobenzoic acid, terpineol, or a mixture of organic solvents which includes at least one of these.

[0119] When the photo-sensitive paste method is used to form the cell walls, the following organic components can be used, for example.

[0120] The organic component contains a photo-sensitive component which is a photo-sensitive monomer, oligomer, or polymer. If necessary, additives such as binders, photo-polymerization initiators, UV absorbents, sensitizers, sensitizing helpers, polymerization prohibitors, plasticizers, thickeners, organic solvents, antioxidants, dispersing agents, or organic or inorganic precipitation preventing agents could be added.

[0121] The photo-sensitive component includes light-insoluble types and light-soluble types. Light-insoluble types include:

(A) ones which contain a functional monomer, oligomer, or polymer that has at least one unsaturated group, etc., in its molecular structure

(B) ones which contain a photo-sensitive compound such as aromatic diazo compound, aromatic azido compound, or organic halogen compound

(C) so-called diazo resins such as condensation of diazo base amine and formaldehyde.

[0122] Light-soluble types include:

(D) ones which contain a complex of organic acid or inorganic salt of diazo compound, quinone diazo group

(E) ones which bind quinone diazo groups with an appropriate polymer binder, such as naphthoquinone of-1,2-diazido-5-ester sulfonate of novolac resin, or phenol.

[0123] All of the above can be used as the photo sensitive component in this invention. For a photo-sensitive paste, (A) is desired because it makes a photo sensitive component which can be easily mixed with the inorganic corpuscle.

[0124] The photo-sensitive monomer is a compound which includes carbon-carbon unsaturated bonding. Specific examples include acrylates such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, sec-butyl acrylate, iso-butyl acrylate, tert-butyl acrylate, n-pentyl acrylate, allyl acrylate, benzyl acrylate, buthoxyethyl acrylate, buthoxy triethylene glycol acrylate, cyclohexyl acrylate, dicyclopentanyl acrylate, dicyclopentenyl acrylate, 2-ethylhexyl acrylate, glycelol acrylate, glycidyl acrylate, heptadecaflorodecyl acrylate, 2-hydroxyethyl acrylate, isobonyl acrylate, 2-hydroxypropyl acrylate, isodecyl acrylate, isooctyl acrylate, lauryl acrylate, 2-methoxy ethyl acrylate, methoxy ethylene glycol acrylate, methoxy diethylene glycol acrylate, octafloropentyl acrylate, phenoxy ethyl acrylate, stearyl acrylate, trifloroethyl acrylate, allylated cyclohexyl diacrylate, 1,4-butane diol diacrylate, 1,3-butylene glycol diacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, polyethylene glycol diacrylate, dipentaerythritol hexa acrylate, dipentaerythritol monohydroxy penta acrylate, ditrimethylol propane tetra acrylate, glycelol diacrylate, methoxidized cyclohexyl diacrylate, neopentyl glycol diacrylate, propylene

glycol diacrylate, polypropylene glycol diacrylate, triglycelol diacrylate, trimethylol propane triacrylate, acryl amide, amino ethyl acrylate, phenyl acrylate, phenoxy ethyl acrylate, benzyl acrylate, 1-naphthyl acrylate, 2-naphthyl acrylate, bisphenol A diacrylate, diacrylate of bisphenol A-ethylene oxide addition product, diacrylate of bisphenolA-propylene oxide addition product, thiophenol acrylate, benzyl mercaptane acrylate, or monomer which replaces 1 to 5 hydrogen atoms in the aromatic rings with chlorine or boron atoms, or styrene, p-methyl styrene, o-methyl styrene, m-methyl styrene, chlorinated styrene, boronated styrene, α-methyl styrene, chlorinated α-methyl styrene, boronated α-methyl styrene, chloromethyl styrene, hydroxy methyl styrene, carboxy methyl styrene, vinyl naphthalene, vinyl anthracene, vinyl carbozol, and one that changes part or all of the acrylate in the molecular structure in the above compounds to methacrylate, γ-methacryloxy propyl trimethoxy silane, 1-vinyl-2-pyrrolidone, etc. In this invention, it is possible to use just one kind or two or more kinds.

[0125] It is possible to improve developing properties by adding unsaturated acids such as unsaturated carbonic acid, etc. Specific examples of unsaturated carbonic acids include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, vinyl acetate, or acid anhydrides of these.

[0126] The amount of these monomers should be 5 to 30 wt. % per total weight of glass powder and photo-sensitive component. Outside this range, pattern formation is difficult or insufficient hardness after curing occurs, which is not desired.

[0127] Suitable binders include polyvinyl alcohol, polyvinyl butyral, ester methacrylate polymer, ester acrylate polymer, ester acrylate-ester methacrylate co-polymer, α-methyl styrene polymer, butyl methacrylate resin, etc.

[0128] In addition, it is possible to use oligomers or polymers attained by polymerization of at least one compound which has the above carbon-carbon double bonding. During polymerization, it is possible to co-polymerize other photo-sensitive monomers so that the amount of these light-reacting monomers will be more than 10 wt. %, preferably 35 wt. % or higher.

[0129] The monomer to be co-polymerized can improve developing properties if it is an unsaturated acid such as unsaturated carbonic acid. Specific examples of suitable unsaturated carbonic acids include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, vinyl acetate, or acid anhydrides of these.

[0130] The acid value (AV) of the polymer or oligomer which has acid groups such as carboxyl groups in side chains as attained should be in the range of 30 to 150, preferably 70 to 120. If the acid value is less than 30, since the solubility of the unexposed (to light) part in the developing solution drops, the concentration of the developing solution is thickened. Because of that, delamination occurs even in the exposed part, and a pattern with high accuracy cannot be attained. On the other hand, if the acid value exceeds 150, the development process window becomes narrow.

[0131] When the developing properties are enhanced by a monomer such as unsaturated acid, keeping the acid value of the polymer less than 50 prevents gelling due to reaction of the glass powder with the polymer, which is desired.

[0132] By adding a photo-reacting group as side chains or end molecules to the polymers or oligomers above, they can be used as photo-sensitive polymers or photo-sensitive oligomers.

The desired photo-reacting groups have ethylene type unsaturated groups such as vinyl groups, allyl groups, acryl groups, methacryl groups, etc.

[0133] Methods for adding these side chains to the oligomer or polymer include the following. An ethylene type unsaturated compound which has a glycidyl group or isocyanate group, chloride acrylate, chloride methacrylate, or acryl chloride is reacted with a mercapto group, amino group, hydroxide group, or carboxyl group in polymer.

[0134] Ethylene type unsaturated compounds which have a glycidyl group include glycidyl acrylate, glycidyl methacrylate, allylglycidyl ether, glycidyl ethyl acrylate, crotonyl glicidyl ether, glycidyl ether crotonate, glicidyl ether isocrotonate, etc.

[0135] Ethylene type unsaturated compounds which have an isocyanate group include (meth)acryloyl isocyanate, (meth)acryloyl ethyl isocyanate, etc.

[0136] The amount of ethylene type unsaturated compound which has a glycidyl group or isocyanate group, chloride acrylate, chloride methacrylate, or acryl chloride added to the mercapto group, amino group, hydroxide group, or carboxyl group should be 0.05 to 1 mol.

[0137] The amount of photo-sensitive polymer in the photo-sensitive glass paste, photo-sensitive oligomer, and binder, should be in the range of 5 to 30 wt. % of the total weight of the glass powder and photo-sensitive component since this makes material which is excellent in pattern formation and sintering shrinkage. Outside this range, pattern formation is impossible, or the pattern will get thicker, which is not desired.

[0138] Specific examples of photo polymerization initiators include benzophenone, o-benzoyl methyl benzoate, 4,40bis(dimethyl amine)benzophenone, 4,4-bis (diethylamino) benzophenone, 4,4-bis (diethylamino) benzophone, 4,4-dichloro benzophone, 4-benzoyl-4-methyl diphenyl ketone, dibenzyl ketone, fluorenone, 2,2-diethoxy acetophenone, 2,2-dimethoxy-2-phenyl-2-phenyl acetophenone, 2-hydroxy-2-methyl propyophenone, p-t-butyl dichloro acetophenone, thioxanthone, 2-methyl thioxanthone, 2-chloro thioxanthone, 2-isopropyl thioxanthone, diethyl thioxanthone, benzyl dimethyl ketanol, benzyl methoxy ethyl acetal, benzoin, benzoin methylether, benzoin butylether, anthraquinone, 2-t-butyl anthraquinone, 2-amil anthraquinone, β-chlor anthraquinone, anthrone, benzanthrone, dibenzo suberone, methylene anthrone, 4-azidobenzal acetophenone, 2,6-bis (p-azido benzilidene) cyclohexanone, 2,6-bis (p-azido benzilidene)-4-methyl cyclohexanone, 2-phenyl-1,2-butadion-2-(o-methoxy carbonyl) oxime, 1-phenyl-propanedion-2-(o-ethoxy carbonyl) oxime, 1,3-diphenyl-propane trion-2-(o-ethoxy carbonyl) oxime, 1-phenyl-3-ethoxy-propane trion-2-(o-benzoyl) oxime, Michler's ketone, 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propanone, 2-benzyl-2-dimethylamino-1-(4-morpholino phenyl)butanone-1, naphthalene sulfonyl chloride, quinoline sulfonyl chloride, N-phenyl thio acrydone, 4,4-azobis isobutylo nitrile, diphenyl disulfide, benzthiazol disulfide, triphenyl phophine, camphorquinone, carbon tetrabromide, tribromophenyl sulfone, benzoin peroxide, and combination of photo-reducing color such as eosin, methylene blue with reducing agent such as ascorbinic acid, or triethanol amine. In this invention, they can be used either alone or in combinations of two or more.

[0139] The amount of photo polymerization initiator is in the range of 0.05 to 20 wt. % per photo-sensitive component. Preferably, it is 0.1 to15 wt. %. If the amount of polymerization initiator is too small, light sensitivity is inferior. If the amount of photo polymerization initiator is too much, !!!!!there is possibility that remaining rate of light-exposing part will be too small.

[0140] Adding UV absorbents is also effective. By adding compounds with high UV absorption; high aspect ratios, high detail, and high resolving power can be attained. As UV absorbents, organic based dyes, especially ones with high UV absorption coefficients in 350 to 450 nm wavelength range are best. Specifically, you can use azo base dye, amino ketone base dye, xanthine base dye, quinoline base dye, anthraquinone base, benzophenone base, diphenyl cyano acrylate base, triazine base, p-amino benzoate base dye, etc. Organic based dye is good since it does not remain in the insulating film after sintering even when it is added as a light-absorbing agent. This prevents a drop in insulating film properties due to the light-absorbing agent. Among these, azo based and benzophenone based are good.
[0141] The amount of organic dye should be 0.05 to 1 wt. % per total weight of the glass powder. If it is less than 0.5 wt. %, the effect of the UV absorbent is low. On the other hand, if it exceeds 1 wt. %, it is not good since insulating film properties after sintering drops. Preferably, it is 0.1 to 0.18 wt. %.
[0142] One example of a method for adding UV rays absorbent which consists of organic dye is going to be explained. First, a solution of organic dye dissolved in organic solvent is prepared beforehand. It is kneaded to make a paste. In another method, glass particles are mixed in the organic dye solution and dried. According to this method, so-called capsule type particles, which have a coating of organic dye on the surface of individual glass particles can be manufactured.
[0143] In this invention, metal such as Ca, Fe, Mn, Co, Mg and oxides included in the inorganic particles may react with the photo-sensitive component in the paste, causing the paste to gel quickly making application impossible. In order to prevent this reaction, a stabilizer should be added to prevent gelling. A triazole compound is suitable, especially benzotriazole derivatives. Among these, benzotriazole is especially effective. One example of surface processing of glass particles by benzotriazole used in this invention is going to be explained. A predetermined amount of benzotriazole based on the weight of the inorganic particles is dissolved in an organic solvent such as methyl acetate, ethyl acetate, ethyl alcohol, methyl alcohol, etc. After that, the particles are immersed in the solution for 1 to 24 hours. After immersing, they are dried naturally preferably at 20 to 30°C to evaporate the solvent, and the particles have been through the triazole process. The amount of stabilizer used (stabilizer/inorganic particles) should be in the range of 0.5 to 5 wt. %.
[0144] A sensitizer is added in order to improve sensitivity. Specific examples of sensitizers include 2,4-diethyl thioxantone, isopropyl thioxantone, 2,3-bis (4-diethyl aminobenzal) cyclopentanone, 2,6-bis(4-dimethyl aminobenzal)cyclohexanone, 2,6-bis (4-dimethyl aminobenzal)-4-methyl cyclohexanone, Michler's ketone, 4,4-bis (diethylamino)-benzophonone, 4,4-bis (dimethylamino) chalcone, 4,4-bis (diethylamino)chalocone, p-dimethyl amino cinnamylidene indoanone, p-dimethyl amino benzylidene indanone, 2-(p-dimethyl aminophenyl vinilene)-isonaphtho thiazol, 1,3-bis (4-dimehyl aminobenzal) acetone, 1,3-carbonyl-bis (4-diethyl aminobenzal) acetone, 3,3-carbonyl-bis (7-diethyl amino coumarin), N-phenyl-N-ethyl ethanol amine, N-phenyl ethanol amine, N-tolyl diethanol amine, N-phenyl ethanol amine, dimethyl amino benzoate isoamyl, diethyl amino benzoate isoamyl, 3-phenyl-5-benzoyl thiotetrazol, 3-phenyl-5-benzoyl thiotetrazol, 1-phenyl-5-ethoxy carbonyl thiotetrazol, etc. In this invention, these can be used either alone or in combinations of two or more kinds.

In addition, some of these sensitizers can be used as photo-polymerization initiators also. When a sensitizer is added to the photo-sensitive paste of this invention, the amount is normally 0.5 to 10 wt. % of the weight of the photo-sensitive component, preferably 0.1 to 10 wt. %. If the amount of sensitizer is too small, improvement of the photo-sensitivity cannot be attained. However, if the amount of sensitizer is too much, !!!!there is possibility that remaining rate of light-exposing part will be too small.

[0145] Furthermore, a sensitizer with good absorption at the wavelength used to expose the paste should be used. In this case, the refractive index becomes extremely high near the absorption wavelength. Therefore, by adding a large amount of sensitizer, the refractive index of the organic component can be improved. The amount of sensitizer in this case is 3 to 10 wt. %.

[0146] A polymerization prohibitor is to improve thermal stability during storage. Specific examples of polymerization prohibitors include hydroquione, monoesterized substances of hydro quionone, N-nitrosodiphenyl amine, phonothiazine, p-t-butyl catechol, N-phenyl naphthyl amine, 2,6-di-t-butyl-p-methyl phenol, chloranil, pyrogallol, etc.

[0147] By using a polymerization prohibitor, the threshold value of the photo-curing reaction goes up. This prevents shrinking of the wall width and thickening of the upper portion of the wall to form gaps.

[0148] The amount of polymerization prohibitor used is normally in the range of 0.01 to 1 weight % based on the total weight of photo-sensitive paste. If it is less than 0.01 wt. %, its will be ineffective. However, if it is more than 1 wt. %, sensitivity drops, and more light will be required to expose the pattern.

[0149] Specific examples of plasticizers include dibutyl phthalate, dioctyl phthalate, polyethylene glycol, glycerin, etc.

[0150] An antioxidant is added to prevent the acryl base co-polymer from oxidizing during storage. Specific examples of antioxidants include 2,6-di-t-butyl-p-cresol, butylized hydroxy cyanisol, 2,6-di-t-4-ethyl phenol, 2,2-methylene-bis-(4-methyl-6-t-butyl phenol), 2,2-methylene-bis-(4-ethyl-6-t-butyl phenol), 4,4-bis-(3-methyl-6-t-buthyl phenol), 1,1,3-tris-(2-methyl-6-t-butyl phenol), 1,1,3-tris-(2-methyl-4-hydroxy-t-butyl phenyl)butane, bis [3,3-bis (4-hydroxy-3-t-butylphenyl) butylic acid] glycol ester, dilauryl thio dipropyonate, triphenyl phosphite, etc. When antioxidant is added, the amount is normally in the range of 0.01 to 1 wt. % of the total weight of the paste.

[0151] The viscosity of the solution can be adjusted by adding an organic solvent to the photo-sensitive paste of this invention if necessary. The organic solvent can be methyl cellosolve, ethyl cellosolve, butyl cellosolve, methyl ethyl ketone, dioxane, acetone, cyclohexanone, cyclopentanone, isobutyl alcohol, isopropyl alcohol, tetrahydro furan, dimethyl sulfoxide, γ-butylo lactone, bromo benzene, chloro benzene, dibromo benzene, dichloro benzene, bromo benzoate, chloro benzoate, or a mixture of organic solvents which contains at least one of these.

[0152] The refractive index of the organic component refers to the refractive index of the organic component of the paste when the photo-sensitive component is exposed to light. That is, when the paste is applied and exposed after the drying process, it means the refractive index of the organic component in the paste after drying. In one method, for example, after the paste

is applied on the glass substrate, the refractive index is measured after drying it for 1 to 30 minutes at 5 to 100°C.

[0153] Measurement of the refractive index in this invention can be done by the ellipsometry method or V block method that is general use. These methods are accurate in confirming the effects of this invention when the measurement is made at the wavelength of light which is used to expose the paste. The refractive index should be measures at a wavelength in the range of 350 to 650 nm. In addition, measurement of refractive index at line i (365 nm) or line g (436 nm) is desired.

[0154] In addition, the refractive index can be measured after the organic component is polymerized by irradiation at the wavelength of the irradiating light. This is similar to the case when the paste is irradiated, only in this case it refers only to the organic component.

[0155] The photo-sensitive paste is normally manufactured by the following method. Various components such as inorganic corpuscles, UV absorbents, photo-sensitive polymers, photo-sensitive monomers, photo-polymerization initiators, glass flits, and solvents, etc., are prepared in a predetermined composition. They are mixed and dispersed uniformly using three rollers or a kneader.

[0156] The viscosity of the paste is adjusted freely according to the amount of inorganic corpuscles, thickening agents, organic solvents, plasticizers, and precipitation preventing agents, etc. The viscosity should be in the range of 2000 to 200,000 cps. For example, when application to the glass substrate is done by spin coating, 200 to 5000 cps is suitable. To acquire 10 to 20 μm film thickness in one application by screen printing, 10,000 to 100,000 cps is desired.

[0157] Next, one example which forms a pattern using a photo-sensitive paste is going to be explained. However, this invention is not limited to only this example.

[0158] Photo-sensitive paste is applied on all or part of the surface of a glass or ceramic substrate, or on a polymer film. Screen printing, bar coating, roll coating, dye coating, or doctor blade coating, etc., can be used. The thickness of the application can be adjusted by selecting the number of applications, screen mesh, and viscosity of the paste.

[0159] Surface treatment of the substrate can be done to improve adhesion when the paste is applied on the substrate. Surface treatment solutions include silane coupling agents such as vinyl trichlorosilane, vinyl trimethoxy silane, vinyl triethoxy silane, tris-(2-methoxy ethoxy) vinyl silane, γ-glycidoxy propyl trimethoxy silane, γ-(methacryloxy propyl) trimethoxy silane, γ (2-aminoethyl) aminopropyl trimethoxy silane, γ-chloropropyl trimethoxy silane, γ-merbaptopropyl trimethoxy silane, γ-aminopropyl triethoxy silane, or organic metal such as organic titanium, organic aluminum, organic zirconium, etc. The silane coupling agent or organic metal is diluted with organic solvent, for example, ethylene glycol monomethylether, ethylene glycol monoethylether, methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, to 0.1 to 5 % concentration. Next, this surface processing solution is applied on substrate uniformly using a spinner, etc. When it is applied on film, there are methods to expose the film after drying, and methods to expose the film after it is applied on a substrate such as glass or ceramic.

[0160] After application, the material is exposed using a light device. Exposure is done by conventional photo lithography method, generally using a photo mask. The mask used is a negative or positive type depending on the type of photo-sensitive organic component. As an

alternative, the desired pattern can be traced directly using a red or blue laser without using a photo mask.

[0161] The light device used to expose the material can be a stepper exposing machine or a proximity exposing machine. In addition, when a large area is exposed, a transport mechanism can be used to transport the substrate with the photo-sensitive paste so that a large area can be exposed using a small exposing machine.

[0162] The light source can be, for example, visible light, near UV, UV, electron beam, X beam, laser, etc. Among these, UV is preferred. For example, a low-pressure mercury lamp, high pressure mercury lamp, super-high pressure mercury lamp, halogen lamp, or sterilizing lamp can be used. Among these, a super high voltage mercury lamp is most suitable. Although exposing conditions differ depending on the film thickness, it is commonly done for 20 seconds to 30 minutes using a super high voltage mercury lamp with 3 to 50 mW/cm^2 output.

[0163] After exposing the film, development is done using the difference in solubility between the photo-sensitive part and non-photo-sensitive part. Immersion methods, shower methods, spray methods, or brushing methods can be used.

[0164] The developing solution is an organic solvent which can dissolve the organic component in the photo-sensitive paste. It is acceptable to add water to the organic solvent as long as its dissolving strength will not be lost. When there is a compound which has an acid group such as a carboxyl group in the photo-sensitive paste, it can be developed by an alkali solution. A metal alkali solution like sodium carbonate such as sodium hydroxide, calcium hydroxide solution can be used. However, an organic alkali solution is better since the alkali ingredients are easily removed during sintering.

[0165] An amine compound can be used as the organic alkali. Specifically, tetramethyl ammonium hydroxide, trimethyl benzyl ammonium hydroxide, monoethanol amine, diethanol amine, etc. can be used. The concentration of the alkali solution is normally 0.01 to 10 wt. %, preferably 0.1 to 5 wt. %. If the alkali concentration is too low, the soluble part is not removed. On the other hand, if the alkali concentration is too high, the pattern bay delaminate or corrosion of the insoluble part may occur. The developing temperature should be 20 to 50 °C for the charging processes.

[0166] Next, sintering is done in a sintering oven . Although the sintering atmosphere and temperature differ depending on the type of paste or substrate, sintering is done in air, nitrogen, hydrogen, etc. A batch type sintering oven or belt type continuous sintering oven can be used.

[0167] When the pattern is formed on a glass substrate, sintering is done for 10 to 60 minutes at 540 to 610°C temperature while increasing the temperature at 200 to 400°C/hr. In addition, although the sintering temperature depends on the glass powder used, sintering should be done at an appropriate temperature where the pattern is not damaged and the shape of the glass powder does not remain.

[0168] If it is sintered at a temperature lower than the appropriate temperature, unevenness of the upper portion of the cell walls and porosity become big, or the lifespan of electric discharge becomes short, or it tends to cause mistaken electric discharge.

[0169] On the other hand, if it is lower than appropriate temperature, shape at formation of pattern is damaged. So, upper portion of parting walls become round, or the wall height will be extremely low, and the desired height cannot be attained.

[0170] Furthermore, an intermediate heating process at 50 to 300°C can be used between the main processes such as exposing, development, and sintering, in order to promote drying or pre-reactions.

[0171]
(examples of practice)

In the following, this invention is going to be explained more specifically using examples of practice. However, this invention is not limited to only these examples. Unless stated otherwise, (%) means weight %. They are indicated in the following:
[0172]
Glass (1):

composition:	Li_2O 7 %, SiO_2 22 %, B_2O_3 32 %
	BaO 4 %, Al_2O_3 22 %, ZnO 2 %
	MgO 6 %, CaO 4 %
Thermal property:	glass transition point 491°C, softening point 528°C
	Coefficient of thermal expansion 74 x 10^{-7}/K
Particle diameter:	D10 0.9 μm
	D 50 2.6 μm
	D 90 7.5 μm
	Maximum particle diameter: 22.0 μm
Relative surface area:	1.92 m^2/g
Refractive index:	1.59 (g line 436 nm)
Relative weight:2.54	

Glass (2)

composition:	Bi_2O_3 38%, SiO_2 7 %, B_2O_3 19 %
	BaO 12 %, Al_2O_3 4 %, ZnO 20 %
Thermal property:	glass transition point 475°C, softening point 515°C
	Thermal expansion coefficient 75 x 10^{-7}/K
Particle diameter:	D10 0.9 μm
	D 50 2.5 μm
	D 90 3.9 μm
	Maximum particle diameter: 6.5 μm

(white filler powder)
Filler: TiO_2, relative weight 4.61

(polymer)
polymer (1): 40 % γ-butylolactone solution of photo-sensitive polymer with 43000 weight average molecular weight, 95 acid value with 0.4 % glycidyl methacrylate (GAM) was reacted with a carboxyl group in a co-polymer which consists of 40 % of methacrylic acid (MAA), 30 % of methyl methacrylate (MMA), and 30 % of styrene (St)

polymer (2): solution of ethyl cellulose / terpineol = 6 / 94 (weight ratio)

(monomer)
monomer (1): X_2-N-CH(CH_3)-CH_2-(O-CH_2-CH(CH_3))$_n$-N-X_2
X:-CH_2-CH(OH)-CH_2O-CO-C(CH_3) = CH_2
n = 2 to 10
monomer (2): trimethylol propane triacrylate·modified PO

(photo polymerization initiator)
IC-369: Irgacure-369 (product by Chiba Gaigy)
2-benzyl-2-dimethylamino-1-(4-morpholinophenyl) butanone-1
IC-907: Irgacure-907 (product by Chiba Gaigy)
2-methyl-1-(4-(methothio)phenyl-2-morpholino propanone

(sensitizer)
DETX-S; 2,4-diethyl thioxantone

(sensitizer helper)
EPA: p-dimethyl amino benzoate ethylester

(plasticizer)
DBP: dibutyl phthalate (DBP)

(thickening agent)
SiO: acetic acid of SiO_2 2-(2-buthoxyethoxy)ethyl 15 % solution

(organic solution)
sudane: azo base organic dye, chemical formula $C_{24}H_{20}N_4O$, molecular weight 380.45

(solvent)
γ-butylolactone
terpineol

(dispersing agent)
Nopcospers 092 (manufactured by Sun Nopco)

(stabilizer)
1,2,3-benzotriazol

example of practice 1

First, photo-sensitive paste for cell walls was manufactured. 100 weight parts of glass powder (glass (1)) with 0.08 weight parts of organic dye was prepared. Next, sudane was dissolved in acetone, a dispersing agent was added, and it was stirred uniformly by a

homogenizer. Next, glass powder was added to this solution. After uniformly dispersing and mixing it using a rotary evaporator, it was dried at 100°C, and the acetone was evaporated. A powder with a uniform surface coating of organic dye was manufactured.
[0173] Polymer (1), monomer (1), photo polymerization initiator (IC-369), sensitizer, plasticizer, solvent were mixed at 37.5 : 15 : 4.8 : 4.8 :2 : 7.5 weight ratio, and they were dissolved uniformly. After that, this solution was filtered using 400 mesh filter, and an organic vehicle was attained.
[0174] The glass powder and organic vehicle above were mixed in a ratio of glass powder:organic vehicle = 70 : 71.6 weight ratio. After they were mixed and dispersed using three rollers, a photo-sensitive paste for cell walls was prepared. The refractive index of the organic component was 1.59; the refractive index of the glass powder was 1.59.
[0175] Next, as in the above, a paste for the dielectric layer with a glass (2):filler:polymer (2) weight ratio = 55 : 10 : 35 was manufactured. This dielectric paste was uniformly applied on a 13 inch glass substrate PD-20 manufactured by Asahi Glass. The electrodes had already been formed with 140 μm pitch, 60 μm linear width, and 4 μm thickness by screen printing using a 325 mesh screen. After that, it was dried for 40 minutes at 80°C. It was temporarily sintered at 550°C to form a 10 μm thick dielectric layer.
[0176] Next, the paste for cell walls was uniformly applied on this dielectric layer by screen printing using a 325 mesh screen and a coating was formed. In order to avoid pinholes in the coating, application and drying were done repeatedly several times, and the film thickness was adjusted. The printing plate for screen printing was shorter than the lengthwise direction of the cell wall pattern. Drying in the middle was done for 10 minutes at 80°C, drying after formation of the coating was done for 1 hour at 80°C. The dry coating thickness was 150 μm. An inclined surface 2000 μm long was formed at the edges of the coating.
[0177] Next, UV from a super high voltage mercury lamp with 50 mJ/cm^2 output was used to irradiate the upper surface through a negatype chrome mask in the shape of stripes 140 μm pitch. Exposure level was 1.0 J/cm^2. A chrome mask with a cell wall pattern longer than the lengthwise direction of the cell walls was used.
[0178] Next, development was done under a shower of 0.2 wt. % solution of monoethanol amine at 35°C for 170 seconds. After that, it was washed with water using a shower spray. By doing so, the part which was not cured was removed, and a stripe shaped cell wall pattern was formed on the glass substrate.
[0179] The glass substrate with the cell wall pattern was sintered for 15 minutes in air at 570°C, and cell walls were formed. The sectional shape of the ends of the cell wall pattern before and after sintering was observed by scanning electron microscope (S-2400 manufactured by Hitachi). The result is shown in table 1. No delamination or swelling is indicated by O; when there was delamination or swelling, the number of occurrences and extent of each were measured and recorded.
[0180] As a result, X was 2 mm, Y was 100 μm, and X/Y = 20 which is within the range specified in this invention. In addition, there was no delamination or swelling at the ends of the cell walls, which was good.
[0181] Next, a luminous paste which emits red, blue, and green light was applied between the cell walls using a screen printing method. These were sintered (30 minutes, 500°C), and a

luminous layer was formed on the sides and bottom of the cell walls, and the back plate was completed.

[0182] Next, the front plate was manufactured according to the following processes. First, ITO was formed on a glass substrate the same as the back plate by sputtering, and resist was applied. After it was exposed and developed in desired pattern, it was etched. A transparent electrode with 0.1μm sintered thickness and 200 μm width was formed. Using a photo-sensitive silver paste which consists of black silver powder, a base electrode 10 μm thick after sintering was formed by photo lithography. The electrodes had 140 μm pitch and 60 μm width.

[0183] A20 μm layer of transparent dielectric paste was applied on the front plate where electrodes had been formed. It was maintained for 20 minutes at 430°C and marked. Next, a 0.5 μm thick MgO film was formed covering the transparent electrodes, black electrode, and dielectric layer using an electron beam vapor deposition machine, and the front plate was completed.

[0184] This front plate was attached to the back plate using paste. Next, the gas for electric discharge was sealed in, the drive circuit was bonded, and the plasma display was manufactured. The display was done by applying voltage to this panel. The results of the evaluation are shown in table 1. When a uniform display was attained over the entire surface, it is describes as O. When problems such as extraneous electrical discharge were seen, its was noted. As shown in table 1, a uniform display was attained over the entire surface.

[0185]

example of practice 2

Except that the photo-sensitive paste for the dielectric layer was made by mixing glass (2), filler, polymer (2), and monomer (2) in a 22.5 : 2.2: 10 : 10 : 0.3 : 1.6 weight ratio, this example was the same as example of practice 1 was done. This dielectric paste was applied on a glass substrate. The dry thickness was 15 μm. Instead of performing temporary sintering, its upper surface was exposed to at 1 J/cm^2 of UV from a super high voltage mercury lamp with 50 m J/cm^2 output. The rest is the same as example of practice 1, and a plasma display was manufactured. The dielectric layer was sintered at the same time as the cell wall pattern. Evaluation was done the same as example of practice 1.

[0186]

example of practice 3

The photo-sensitive paste for cell walls was applied on the substrate by screen printing 50 μm thickness over an area larger than the length of the cell wall pattern on the photo mask. Next, a screen printer smaller than the length of cell wall pattern on the photo mask was used to print a 100 μm thick film. Except for these changes, this example was the same as example of practice 1.

[0187] When the cell wall pattern was formed, the lower part of the cell walls with 5 μm thickness formed a right angle. The upper part of the cell walls with 100 μm thickness was inclined. This shape is shown in figure 14.

[0188] When it was sintered as in example of practice 1, the lower part (33 μm height after sintering) rose up 10 μm. However, the ends of the upper part (67 μm height after sintering)

did not rise up. Since The upper part was 67 μm high, the lower part did not rise up more than the height of the upper part. As a whole, the cell walls were formed without problems. After that, a plasma display was manufactured the same as in example of practice 1, and evaluation was done. The results are shown in table 1.

[0189]
example of practice 4

The paste for cell walls was applied to the substrate 250 μm thickness before drying using a slit dye coater. Before drying a nozzle with 0.4 mmϕ inner diameter was used to propel air to form an inclined surface on the edge of the coating. Except for these changes, the cell wall pattern was formed the same as example of practice 1. Air pressure was 2.5 kgf/cm^2; the nozzle was perpendicular to the substrate in one direction and inclined at 45° in the other direction. Later, a plasma display was manufactured the same as example of practice 1, and evaluation was done. The results are shown in table 1.

[0190]
example of practice 5

The inclined surface was formed on the edge of the coating using an air pressure of 0.5 kgf/cm^2. Except for this change, a plasma display was manufactured the same as example of practice 4, and evaluation was done. The results are shown in table 1.

[0191]
example of practice 6

The paste for cell walls was applied on the substrate and dried at 80°C for 5 minutes. Next, a solvent of ethyl cellulose/terpineol = 1/99 (weight ratio) was propelled from a nozzle with 1.5 mmϕ inner diameter at a pressure of 1.0 kg/cm^2, and an inclined surface was formed at the edges of the coating. Except for this change, a plasma display was manufactured the same as example of practice 4, and evaluation was done. The results are shown in table 2.

[0192]
example of practice 7

When the inclined surface was formed on ends of coating, propelling was performed using a 0.4 mm slit. Except for this change, a plasma display was manufactured the same as example of practice 4, and evaluation was done. The results are shown in table 2.

[0193]
example of practice 8

When the inclined surface was formed on the edges of the coating film the coating was dried at 80°C for 1 hour. Next the inclined surface was formed by scraping the edges of the coating with a knife. Except for this change, a plasma display was manufactured the same as example of practice 4, and evaluation was done. The top edge of the knife was ϕ = 30 degree. This knife was angled at Θ = 45 degree over the substrate. 15 μm was removed with each cut

at 5 m/s. This operation was repeated 5 times, and 75 μm was removed from the upper part of the cell walls. The results are shown in table 2.

[0194]
example of practice 9
First, a stripe shaped cell wall mold with 200 μm pitch, 30 μm linear width, and 200 μm height was formed on an aluminum substrate using a grinder. Next, silicon resin was used to fill the mold, and a silicon mold 300 mm square with a stripe shaped pattern with 200 μm pitch, 30 μm linear width, and 200 μm height was manufactured and used as a mother mold for the cell walls. By forming the inclined part on the ends of the cell walls in the original mold, a 3 mm long inclined part was formed at the ends of the silicon mother mold.
[0195] Next, 800 g of glass powder (1), 200 g of polymer(2), 50 g of plasticizer, and 250 g of terpineol were mixed and dispersed using three rollers, and a paste for cell walls with 9500 cps viscosity was manufactured.
[0196] Next, this paste for cell walls was used to fill the silicon mold using a doctor blade coater. After that, it was transferred to a 400 mm square glass substrate. The silicon mold was released, and a cell wall pattern was formed. Next, the glass substrate and the cell wall pattern was sintered under the same sintering conditions as in example of practice 1, and the cell walls were formed.
[0197] After that, a plasma display was manufactured the same as example of practice 1, and evaluation was done. The result are shown in table 2.

[0198] example of practice 10
First, stripe shaped grooves with 200 μm pitch, 30 μm linear width, and 200 μm height were formed on a 1mm thick copper plate by etching method to form a mother mold for cell walls. Etching was done so that an inclined surface was formed at ends of the grooves.
[0199] Next, 800 g of glass powder (1), 150 g of polymer(2), 50 g of plasticizer, 100 g of monomer (2), 10 g of polymerization initiator (benzoyl oxide), and 250 g of solvent were mixed and dispersed using three rollers, and a paste for cell walls with 8500 cps viscosity was manufactured.
[0200] Next, this paste for cell walls was used to fill the mother mold for cell walls using a doctor blade coater. After that, it was pressed on a 400 mm square glass substrate and heated to 100°C for 30 minutes. Next, the mother mold for cell walls was released, and a cell wall pattern was formed. Next, the glass substrate with the cell wall pattern was sintered under the same sintering conditions as example of practice 1, and cell walls were formed.
[0201] After that, a plasma display was manufactured the same as example of practice 1, and evaluation was done. The results are shown in table 2.

[0202]
example of practice 11
First, stripe shaped grooves with 200 μm pitch, 30 μm linear width, and 200 μm height were formed on a 1mm thick copper plate by etching to form a mother mold for cell walls. Etching was done so that a 10 degree incline would be formed at the ends of the grooves.

[0203] Next, the paste for cell walls in example of practice 10 was applied on the substrate the same as example of practice 4. Before drying, the mother mold for cell walls was pressed onto the paste for cell walls on the glass substrate. While still under pressure, it was heated to 80°C. Next, the mother mold for cell walls was released, and a cell wall pattern was formed. Next, the glass substrate with the cell wall pattern was sintered under the same sintering conditions as example of practice 1, and cell walls were formed.
[0204] After that, a plasma display was manufactured the same as example of practice 1, and evaluation was done. The results are shown in table 3.

[0205]
example of practice 12

Example of practice 12 was the same as example of practice 1 except that after the photo-sensitive paste for cell walls was applied and dried, the ends of the photo-sensitive paste for cell walls was rubbed with a cloth impregnated in solvent to form an inclined surface. A plasma display was manufactured the same as example of practice 1, and evaluation was done. The results are shown in table 3.

[0206]
example of comparison 1

An edge tool with an angle ϕ was used to form an 80 degree inclined surface at ends of coated layer which was 35 μm long. Except for this change, the same procedures as example of practice 8 were done, and a cell wall pattern was formed.
[0207] Since this paste would shrink to 63 % during sintering, if there is no delamination or swelling, the sintered shape will be X = 35 μn, Y = 100 μm, and H/Y = 0.35 after sintering.
[0208] As a result of sintering under the same conditions as example of practice 1, 80 μm delamination was produced at the ends of the cell walls. After that, a plasma display was manufactured the same as example of practice 1, and evaluation was done. The results are shown in table 3. Cross talk was generated in the range of approximately 10 mm width around the display surface.

[0209]
example of comparison 2

Except that a chrome mask smaller than the lengthwise direction of the cell walls was used, a cell wall pattern was formed the same as example of practice 1. The ends of the cell wall pattern were vertical, and there was no inclined part.
[0210] When it was sintered under the same conditions as example of practice 1, there was 20 μm swelling at the ends of the cell walls. This shape of the ends of the cell walls is shown in figure 5. After that, a plasma display was manufactured the same as example of practice 1, and evaluation was done. The results are shown in table 3. Cross talk was generated in the range of approximately 10 mm width around display surface.

[0211]
Table 1

		Ex of pract 1	Ex of pract 2	Ex of pract 3	Ex of pract 4	Ex of pract 5
Before sintering	X' (μm)	2000	3000	2000	2000	2000
	Y' (μm)	150	150	100	120	60
	Coating thickness (μm)	150	150	150	150	150
	Y'/coating thickness	1	1	0.67	0.53	0.4
After sintering	X (μm)	2000	3000	2000	2000	2000
	Y (μm)	100	100	67	80	40
	X/Y	20	30	29.9	25	50
	Maximum angle (degrees)	60	55	55	2.3	1.1
Cell wall ends		O	O	O	O	O
Delamination height(Height of swelling)(μm)		0	0	0	0	0
Electric discharge result		O	O	O	O	O

[0212]
Table 2

		Ex of pract 6	Ex of pract 7	Ex of pract 8	Ex of pract 9	Ex of pract 10
Before sintering	X' (μm)	4000	500	130	2400	2000
	Y' (μm)	75	150	75	200	200
	Coating thickness (μm)	150	150	150	200	200
	Y'/coating thickness	0.5	1	0.5	1	1
After sintering	X (μm)	4000	500	130	2400	2000
	Y (μm)	50	100	50	120	100
	X/Y	80	5	2.6	20	20
	Maximum angle (degrees)	0.7	11.3	30	2.9	2.9
Cell wall ends		O	O	O	O	O
Delamination height(Height of swelling)(μm)		0	0	0	0	0
Electric discharge result		O	O	O	O	O

[0213]
table 3

		Ex of pract 11	Ex of pract 12	Ex of comp 1	Ex of comp 2
Before sintering	X' (μm)	570	5000	35	0
	Y' (μm)	200	150	150	-
	Coating thickness (μm)	200	150	150	150
	Y'/coating thickness	1	1	1	-
After sintering	X (μm)	570	5000	Unable to measure	Unable to measure
	Y (μm)	100	100	Unable to measure	Unable to measure
	X/Y	5.7	50	Unable to measure	Unable to measure
	Maximum angle (degrees)	10	1.1	80	Unable to measure
Cell wall ends		O	O	delamination	swelling
Delamination height(Height of swelling)(μm)		0	0	80	20
Electric discharge result		O	O	Cross talk at edge	Cross talk at edge

[0214]
(Effects of this invention)

By shaping the ends of the cell walls as described in this invention, a plasma display free of delamination or swelling of the cell walls can be attained. Because of this, it is possible to offer a plasma display which is uniform over its entire surface which does not generate extraneous electrical discharge at the edges. The plasma display in this invention can be used for big screen TV's or computer monitors.

(Simple explanation of figures)
Figure 1: Structure of a plasma display.
Figure 2: side view of the cell walls in this invention.
Figure 3: side view of former cell walls.
Figure 4: side view of delamination of the cell walls after sintering.
Figure 5: side view of swelling of the cell walls after sintering.
Figure 6: side view which shows one example of the cell wall shape in this invention.
Figure 7: side view which shows one example of the cell wall shape in this invention.
Figure 8: side view which shows one example of the cell wall shape in this invention.
Figure 9: section which shows one example of the inclined surface formed on the coating of paste for cell walls.

Figure 10: section which shows the relationship between the shape of the edge tool or grindstone and the shape of the edge of coating formed by these.
Figure 11: one example of forming the inclined surface using an edge tool which is a desirable manufacturing method in this invention.
Figure 12: one example of forming the inclined surface using an edge tool which is a desirable manufacturing method in this invention.
Figure 13: section of a mother mold for cell walls which is used in the manufacturing method in this invention.
Figure 14: section of a cell wall pattern where the inclined surface has been formed at edge of the coating in example of practice 3.